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BY THE
KJELDAHL TECHNIQUE

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ESTIMATION OF CLEAN WOOL BY THE KJELDAHL TECHNIQUE

By
George C. LeCompte [1] and Henry H. Lipp [2]
Livestock Division Wool Laboratory, Agricultural
Marketing Service, Denver 2, Colo.

INTRODUCTION

The generally accepted method for determining the clean wool content of a sample of grease wool consists of scouring the wool, drying the scoured product, and then analyzing the dried scoured vegetable matter content, and alcohol extractives content. The clean wool content is determined by subtracting the total of the above-mentioned non-wool percentages from 100% and adjusting the scoured weight to a standard 14% content of non-wool components. Of course, each of these analytical methods presents its amount of work involved and each determination carries along with it its own experimental errors. This procedure for determining clean wool by measuring in four separate tests the amount of all the non-wool components present seemed somewhat complicated when it was considered that the amount of wool present might be obtained in one determination of the nitrogen present in the sample by the Kjeldahl technique.

Any Kjeldahl method for estimating the amount of clean wool would have to proceed on the fundamental assumption that all clean wools, regardless of origin, would have a substantially constant nitrogen content. Barritt (2) found fairly constant nitrogen contents for typical wools, with an average value of 16.70%, and a range of 15.85% to 17.07%. However, this disagreed somewhat with Gortner (3) who had found 16.27% nitrogen in white wool. Later, Winton and Edgar (9) found 29 samples with an average of 16.11% and a range of nitrogen content of 15.81% to 16.35%. Von Bergen and Mauersberger (7) reported values ranging from 16.10% to 16.51%. It appeared advisable to see if relatively rapid and easy methods of nitrogen determination on wool could be devised, and if so to apply these methods in an attempt to establish with greater certainty the nitrogen content of wool.

Considerable work was carried out on pure chemicals in an effort to arrive at rapid digestion methods. With satisfactory digestion methods arrived at, it was decided to use an adaptation of the hypobromite oxidation technique of Willard and Cake (8) to determine the amount of nitrogen present in the digest. This method, although possessed of some disadvantages, proved to be acceptable in analyzing digestions of pure chemicals or of small wool samples. The next problem was that of adapting these digestion and nitrogen determination methods to the practical and statistical demands in the determination of nitrogen in wool samples, both for the research needs of this paper and the practical needs of routine wool analysis in laboratories. A method of nitrogen determination accurate to 0.01 mg. would be useless if it had to be restricted to 0.25-gram samples of wool which themselves might vary by several percent in their content of non-wool components. The answer was given by a technique in which 50-gram wool samples could be practically instantaneously hydrolyzed and dissolved by pouring upon them 500 ml. of boiling 60% (by volume) sulfuric acid. From this solution there could be obtained the necessary small-sized aliquots which still accurately represented 50-gram wool portions which were free from the serious sampling error troubles of 0.25-gram samples. These methods were applied to various pure chemicals and thoroughly cleaned wool samples.

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[1] George C. LeCompte was formerly with the Livestock Division Wool Laboratory.

[2] Mr. Lipp is now with the Geologic Division, Geochemistry and Petrology Branch, Chemistry Group, Department of the Interior, Denver 2, Colo.

EXPERIMENTAL DETAILS

(a) Preparation of Wool Samples. Twenty-five assorted wool samples were processed. Efforts were made to get the samples as clean and uniform as possible. They were given a double dusting in a Wilson-type duster, gross impurities such as vegetable matter, taggy patches, or paint being picked out and discarded.

Portions of the picked and opened wool above were weighed out to 300 grams or less, then scoured in rectangular scouring screens 34 x 42 x 18 cms. deep. The scouring ratio, grams scouring liquor to grams grease wool, at all times was greater than 83 to 1. The scouring solution consisted of 0.75% sodium carbonate, 0.075% detergent, and was held at 60° C. The detergent was nitrogen free. Two scouring baths in fresh liquor were given, then one bath in rinse water at 50° C. Each bath lasted for one minute while the sample received 24 strokings. The bottom and the sides of the scouring screens consisted of perforated metal, so the impurities could easily diffuse away from the sample. After the rinse the samples were centrifuged and then dried in a steam-heated dryer with efficient air circulation. The dried samples were allowed to stand in the open air overnight. They were then subjected to an exhaustive hand-picking and hand-blending process, each tuft being picked up, examined, picked free of the great bulk of impurities, then broken into several smaller tufts which were distributed evenly over a table top. During the picking as much dust as possible was made to drop out of the sample. The entire sample was processed in this fashion, producing a sample uniform and low in content of ash, vegetable matter, and extractives. The sample was then allowed at least 24 hours air conditioning to assure that its moisture content was uniform.

(b) Analysis of the Samples. Each sample, though very uniform and low in contents of ash, vegetable matter, and extractable impurities, still contained unknown quantities of these components. Our preliminary experiments had indicated that the nitrogen contents of the wool samples should be open to accurate measurement. It was felt necessary to relate these nitrogen contents to moisture-free, ash-free, vegetable-matter-free and extractives-free wool weights. Every effort was made to obtain accurate determinations for these non-wool components.

Moisture determination by oven drying is not absolute so the drying methods recommended by the ASTM (1) were not used. Moisture was determined on 50-gram samples by toluene distillation (5), the distillation being continued for three hours, or longer, until there was no further increase in the moisture reading in the trap. The method and apparatus was standardized against known amounts of water.

Ash was determined on 20-gram samples by first burning the wool off with Meker burners, then igniting until carbon-free in an electric furnace at 600° C. (6).

Vegetable matter was determined on 20-gram samples according to the method recommended by the ASTM (1), a modification of the method put forth by LeCompte and Coe (4). The wool samples were dissolved by pouring boiling 10% sodium hydroxide over them. The constitution by type of vegetable matter was estimated visually. The vegetable matter was filtered off on fine cheese cloth, dried, weighed, ashed and the weight of ash deducted from the dried weight of the sample. This net weight, multiplied by the factor determined by the type of vegetable matter, gave the weight of bone-dry vegetable matter in the sample.

Extractable matter was determined by extracting 10-gram samples to completion with ethanol in Soxhlet extractors (at least 6 hours), evaporating the alcohol and weighing the extracts.

All analyses and weighings were so conducted that the analytical results were felt to be accurate in the range of hundredths of a percent. A typical total analysis follows: Duplicate moistures, 11.85% and 11.89%; duplicate ashes, 0.88% and 0.89%; duplicate vegetable matters, 0.03% and 0.03%, duplicate extracts, 1.03% and 0.98%. The average values of each component were totaled and the total subtracted from 100.00% to give a factor expressing the percentage of absolutely dry and clean wool which was to be subjected to the nitrogen determination methods.

(c) Preparation of Hydrolyzed Wool Solutions. In a 1-liter beaker place a 50-gram sample of the wool which has been analyzed as above. In a separate beaker pour 300 mls. concentrated H_2SO_4 into 200 mls. H_2O. Care! Pour this hot mixture on the wool sample and stir. The wool sample will be completely dissolved in two minutes. Cool and filter through a fine mesh stainless steel screen into a 1-liter volumetric flask. The vegetable matter caught on the screen should be thoroughly rinsed with water and any material rinsed from it filtered into the flask. Dilute the dissolved wool sample with cold water. Thoroughly stir and cool until the solution reaches the 1-liter mark.

(d) Digestion of Hydrolyzed Wool Aliquots or Samples of Pure Chemicals. The procedure described hereafter provides for the digestion of 50 ml. aliquots of the hydrolyzed wool sample, equivalent to 2.5 grams of the original wool, or of samples of pure chemicals equivalent to about 380 mgs. of nitrogen. Digestion of 50 ml. aliquots requires 30 to 40 minutes. The digestion is diluted in a volumetric flask, and the final nitrogen determination is run on a 10% aliquot amounting to 0.25 grams of the original wool. However, 5 ml. aliquots of the original hydrolyzed wool sample, equivalent to 0.25 grams of the original wool, or 38 mgs. of nitrogen could be digested in 10-20 minutes and tested directly.

Pipette 50 mls. of the hydrolyzed wool solution into a 500 ml. Kjeldahl flask. This contains the equivalent of 2.5 grams of the original wool and also contains 15 mls. concentrated H_2SO_4. Add 5 mls. concentrated H_2SO_4, 2 mls. 1% H_2SeO_3, and heat vigorously until all water has evaporated and the sulfuric acid is condensing on the walls of the flask. Continue the vigorous heating for at least five minutes. (If this initial digestion with H_2SO_4 alone is not thorough, the succeeding addition of and digestion with K_2SO_4 will cause troublesome foaming.) Add 10 grams K_2SO_4, and continue heating vigorously with H_2SO_4 condensing on the walls and neck of the flask, until the digestion has become pale yellow in color. Cool, add 2.5 grams of potassium persulfate ($K_2S_2O_8$), mix by swirling and heat until no more bubbles of oxygen are evolved. Cool and mix with 150-200 mls. cold water. Neutralize with 5N sodium hydroxide solution (while keeping cool), until almost at the Methyl Red yellow end point, and transfer and dilute to the 500 ml. mark in a half liter volumetric flask.

(e) Determination of Ammonia in Neutralized Digestions. Pipette into a 500 ml. Erlenmeyer flask 50 ml. of the digested hydrolyzed wool sample. Add 10 mls. of 30% (30 gms./100 mls.) sodium bromide solution. Pipette in exactly 20.00 mls. of approximately 0.6N sodium hypochlorite, which has been made approximately 0.2N with sodium hydroxide. (Some of the 5% sodium hypochlorite solutions sold in grocery stores furnish an excellent source of material).

At the same time in two similar standardizing setups the same quantities of sodium hypochlorite solution are pipetted into a known quantity of ammonium chloride in one flask, and into a blank determination on the reagents in another flask. As soon as the hypochlorite has been added to the sample and to the standardizing setups, the contents of the flasks are mixed by swirling and set aside in the dark so that the reaction can proceed to completion. Tests indicated that the reaction was complete at 5 minutes although it might have been completed in a still shorter time. There is then added 100 mls. of cold water, 50 mls. of 10% potassium iodide solution, and 5 mls. of 12 N hydrochloric acid to each of the flasks. Immediately back titrate the liberated iodine with approximately 0.6N thiosulfate to a pale yellow color, add 1 ml. of 2% starch solution and continue the back titration until the blue color of the starch end point just disappears. The difference between the amount of standard thiosulfate required for the hypochlorite, with and without the sample being present, is a measure of the nitrogen.

EXPERIMENTAL FINDINGS

The above procedures were applied to several pure chemicals and to twenty-five samples of wool. The results are recorded in Table 1.

DISCUSSION

The results recorded in Table 1 on pure chemicals demonstrate that the digestion and nitrogen determination methods used furnish acceptable accuracy. Notice that complete nitrogen values were found on tyrosine, a difficult compound to digest. The digestions were finished in 40 minutes or less, the amount of materials digested contained about 380 milligrams of nitrogen. Complete digestions could be obtained in 10 to 20 minutes when the sample size was reduced to about 38 milligrams nitrogen, (0.25 grams wool).

Four nitrogen determinations were run upon a sample of Chinese Cashmere, but the results of 17.37, 17.38, 17.27, and 17.27% are not thought to be reliable. These values are considered unreliable, not because of any uncertainty in the nitrogen determinations, but because one of the other analytical methods failed. The cashmere wool even after a thorough scouring, hand opening, and hand dusting, was filled with flakes of a hard dry material similar to dandruff. In the vegetable matter analysis, these flakes did not dissolve in the boiling sodium hydroxide solution, but filtered off and were weighed with the vegetable matter. They were protein in nature and the final effect of these flakes of epidermis was to improperly increase the nigrogen finding on the Chinese Cashmere sample.

Table 1.--Percent of nitrogen found in various wools and pure chemicals

	Percent nitrogen found					Percent nitrogen
Sample	Test 1	Test 2	Test 3	Test 4	Ave.	Theory
Acetanilide	10.36	10.36	10.35	10.46	10.38	10.36
Tyrosine	7.69	7.81	7.70	7.72	7.73	7.73
Alanine	15.63	15.75	15.65	15.64	15.67	15.72
Argentine 3/8 Blood	17.00	16.95	16.94	16.98	16.97	
Brazil Fine	16.98	16.93	16.98	17.10	17.00	
Uruguay 1/4 Blood	17.18	17.16	17.08	17.12	17.14	
Australian Fine	16.63	16.65	16.69	16.86	16.71	
New Zealand Low $\frac{1}{4}$ Blood	16.65	16.67	16.92	16.98	16.81	
China Cashmere	(17.37)*	(17.38)*	(17.27)*	(17.27)*	(17.32)*	
Average Foreign Wools					16.93 1/	
Idaho Fine	17.10	17.06	17.13	17.06	17.09	
Idaho 1/2 Blood	17.01	17.16	16.85	17.09	17.03	
Idaho 1/4 Blood	16.98	16.96	17.02	17.05	17.00	
Maryland 3/8 Blood	17.04	16.82	16.94	16.92	16.93	
California Fine	16.73	16.95	16.86	16.81	16.84	
California 3/8 Blood	16.94	17.06	16.94	16.79	16.93	
California Low $\frac{1}{4}$ Blood	16.81	16.89	16.88	16.89	16.87	
Tennessee Fine	16.93	16.92	-	-	16.93	
Tennessee 1/4 Blood	16.93	16.88	-	-	16.91	
Ohio 3/8 Blood	16.84	16.82	16.86	16.88	16.85	
Ohio 1/4 Blood	16.91	16.87	-	-	16.89	
Minnesota 3/8 Blood	16.95	16.93	-	-	16.94	
Minnesota 1/4 Blood	16.84	16.83	-	-	16.84	
Colorado Fine	16.80	16.79	16.85	16.87	16.83	
Colorado 1/2 Blood	16.86	16.86	16.91	16.83	16.87	
Colorado 3/8 Blood	16.82	16.95	16.92	16.92	16.90	
Colorado 1/4 Blood	16.62	16.67	16.87	16.78	16.74	
N. Dakota 3/8 Blood	16.77	16.72	-	-	16.75	
N. Dakota 1/4 Blood	16.76	16.78	16.79	16.85	16.80	
Average U. S. Wools					16.89	
Average All Wools					16.90	

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*These values not considered reliable

1/ China Cashmere value not included in this average

United States wools and foreign wools presented much the same picture on average and range of nitrogen contents. The foreign wools averaged 16.93% nitrogen content and had a range of 16.71% to 17.14% while the United States wools averaged 16.89% nitrogen content, and had a range of from 16.75% to 17.09%.

It would appear proper to accept 16.90% as the best average figure for the nitrogen content of absolutely dry, absolutely clean wool. However, different wools may vary from this figure, at least within the range of 16.71% to 17.14%. Statistical analysis of the data indicated that these variable nitrogen contents were a real property of the wool samples and could not be explained on the basis of experimental or sampling error.

The average value of 16.90% nitrogen content found here agrees rather well with Barritt's average findings on typical wools of 16.72%. Our higher findings are probably due to our use of an absolute determination of moisture, to our introduction of tests for vegetable matter and ash, and to our extraction to completion with ethyl alcohol, all of which would operate to decrease the apparent amount of clean wool to which a given nitrogen finding could be compared, and thus to increase nitrogen content findings. Assuming these processes resulted in increased findings for moisture of 0.3%, for ash of 0.5%, for vegetable matter of 0.1%, and for extractives of 0.2%, all of which assumptions appear probable, we believe the comparative situation can be summarized in the two calculations below:

$$\frac{(16.72 \text{ gms. } N_2)(100)}{(100 \text{ gms. wool not analyzed})} = 16.72\% \ N_2 \text{ Content}$$

$$\frac{(16.72 \text{ gms. } N_2)(100)}{(100 \text{ gms. wool})\ (1-0.003 \ H_2O - 0.005 \text{ Ash} - 0.001 \text{ VM} - 0.002 \text{ Ext.})} = 16.90\% \ N_2 \text{ Content}$$

Accepting 16.90% as the best figure for the average nitrogen content of wool, the factor to convert percent nitrogen to the A.S.T.M. definition for standard clean wool (wool containing a total of 14% moisture and other non-wool components) becomes: (100)(100)/(16.90))100-14), or 6.88042. The total standard deviation of the quadruplicate tests on wool in Table 1 is 0.135% nitrogen content. The factor converts this to 0.93% standard clean wool. For a probability of 95% the limits of error then become (1.96)(0.93) = ±1.82% on a clean wool. For a test on a 50% yield grease wool these limits of uncertainty reduce to ±0.91% clean wool content. The method of test could be worked up to be rapid and convenient but apparently could not be made to be more accurate on U. S. wools than ±0.91% clean wool content, for a probability of 0.95.

SUMMARY

A method of nitrogen determination applicable to 50-gram wool samples has been described. The procedure involves a practically instantaneous dissolving of the wool sample in boiling 60% (by volume) H_2SO_4, aliquoting the solution, a rapid digestion of the aliquot, and a determination of nitrogen in an aliquot of the digest by oxidation with sodium hypobromite. Various wools were found to vary in nitrogen content from 16.71% to 17.14%, with an average value of 16.90%.

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